A Mean Field Approximation of the Excluded Volume Effect in Polymer Solutions (Commemoration Issue Dedicated to Professor Hiroshi Ibagaki, Professor Michio Kurata, Professor Ryozo Kitamura, On the Occasion of Their Retirments)

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The extension of a linear polymer chain is discussed in a mean field approximation. The average segment density $\rho(r)$ at the distance r from one end of the chain is determined by the energy balance equation, where the diffusional interaction caused by segmental Brownian motions should be taken into consideration in the case of weaker excluded volume effect. This interaction term can be substituted by an effective field potential, and the screening of excluded volume in the semidilute region is also discussed with the aid of the effective potential concept.

KEY WORDS: Mean field approximation/ Excluded volume effect/ Polymer solutions/ Segmental diffusional interaction/

1. Introduction

The extension R, i.e. the root mean square end-to-end distance, of an isolated linear polymer, which is composed of N consecutive segments, is expressed in a good solvent as

$$R \sim N^{\nu}, \tag{1.1}$$

where the exponent ν, originally derived by Flory,[1] is given by

$$\nu = 3/(d+2) \tag{1.2}$$

in the space of the dimensionality d.[2] The self-consistent field method[3] or the mean field theory[4] to describe the excluded volume effect led also to the same exponent. Recently the renormalization group method has given a very close value to the exponent.[5]

In a semidilute solution of the segment concentration c, the scaling concept[6] indicates, by making use of a scaling parameter c/c^*, the c-dependence of R to be

$$R \sim N^{\nu}(c/c^*)^{-x}, \tag{1.3}$$

where

$$c^* \sim N^{1-\nu d} \tag{1.4}$$

is the segment concentration in an isolated polymer. Owing to the excluded volume screening, which is caused by intervening segments of other polymer chains, Eq. (1.3) should give the N-dependence of R just like a Gaussian chain as

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$$R \sim N^{1/2}. \tag{1.5}$$

This leads straightforwardly to the exponent

$$x = \frac{2\nu - 1}{2(\nu d - 1)} = \frac{4 - d}{4(d-1)}. \tag{1.6}$$

Eqs. (1.2) and (1.6) indicate that the excluded volume effect vanishes at $d=4$.

As an interpretation of the c-dependence of R, which is given by eqs. (1.3) and (1.6), the blob concept has proven to be useful. The number of consecutive segments n per blob, in which the excluded volume is effective, is determined by

$$c \sim n^{1-\nu d} \tag{1.7}$$

and the polymer chain, as a whole, behaves like a Gaussian chain composed of N/n consecutive blobs of the size $\sim n^{\nu}$ as

$$R \sim n^{\nu}(N/n)^{1/2} \sim N^{1/2} c^{-\frac{4-d}{4(d-1)}} \tag{1.3'}$$

Since the blob concept is not the sole interpretation, in the present article a mean field concept will be extended to understand the excluded volume screening.

2. Mean Fields in Polymer Solutions

For mathematical simplicity, the number of segmentes s, which are numbered from one end of a linear chain, is regarded as a continuous variable. Let be the end of the chain located at the origin. Then, the consecutiveness of segments in the chain requires on the average

$$\frac{ds}{dr} \sim r^{d-1} \rho(r), \tag{2.1}$$

where $\rho(r)$ is the segment density, at the position distant r from the origin, of the chain under consideration. The dimensionless energy integral[4] per unit ds results in

$$\left(\frac{dr}{ds}\right)^2 - \phi + \frac{d\psi}{ds} = 0, \tag{2.2}$$

where the first term shows the short range interaction caused by adjacent segments, the second term the long range interaction caused by remote segments, and the last term the diffusional interaction caused by segmental Brownian motions.

2.-1. *Dilute Solution*

In the dilute region, we have the excluded volume potential as

$$\phi \sim v\rho(r), \tag{2.3}$$

where v is the excluded volume parameter, and

$$\psi \sim \ln \rho \tag{2.4}$$

since the diffusional interaction simply originates from non-uniformity in $\rho(r)$.

For good solvents, the ϕ term predominates over the $\frac{d\psi}{ds}$ term in Eq. (2.2). Therefore, with the aid of Eqs. (2.1) and (2.3), we have

$$\rho(r)\sim v^{-1/3}r^{-2(d-1)/3}, \tag{2.5}$$

and we obtain from Eq. (2.1)

$$N=\int_0^R \frac{ds}{dr}\,dr\sim v^{-1/3}\int_0^R r^{(d-1)/3}\sim v^{-1/3}R^{(d+2)/3} \tag{2.6}$$

in accordance with Eqs. (1.1) and (1.2).

For the θ-solvent, on the contrary, the $\frac{d\psi}{ds}$ term remains instead of the ϕ term in Eq. (2.2). With the aid of Eqs. (2.1) and (2.4) we have

$$\rho(r)\sim r^{-(d-2)} \tag{2.7}$$

and

$$N\sim\int_0^R r^{d-1}\rho(r)\,dr\sim R^2, \tag{2.8}$$

which is in accordance with Eq. (1.5). The crossover from the θ regime to the good solvent regime takes place at

$$v_c\sim N^{-(4-d)/2}. \tag{2.9}$$

If we are to substitute $\frac{d\psi}{ds}$ by an effective field potential, expressed as a function of $\rho(r)$, we must have in order to obtain Eq. (2.8)

$$\phi\sim\{\rho(r)\}^{2/(d-2)} \tag{2.10}$$

which gives the same ρ-dependence as Eq. (2.3) at $d=4$.
It should be emphasized that the $\frac{d\psi}{ds}$ term or the equivalent potential (2.10) is indispensable in the case of weaker excluded volume effect.

2.-2. *Semidilute Solutions*

In the semidilute region, at present we have no adequate approximation for the diffusional interaction ψ. Therefore, we assume, by the aid of a scaling parameter ρ/c, the long range interaction is screened as

$$\phi\sim v\rho(\rho/c)^y. \tag{2.11}$$

Since this should play a role of the effective potential, Eq. (2.11) is expected to have the same ρ-dependence as Eq. (2.10), and it leads to

$$y=\frac{4-d}{d-2}. \tag{2.12}$$

Then, Eqs. (2.11) and (2.12) result in

$$\rho(r)\sim v^{-\frac{d-2}{2(d-1)}}c^{\frac{4-d}{2(d-1)}}r^{-(d-2)} \tag{2.13}$$

and

$$N \sim \int_0^R r^{d-1} \rho(r)\, dr \sim v^{-\frac{d-2}{2(d-1)}} c^{\frac{4-d}{2(d-1)}} R^2 \tag{2.14}$$

in accordance with Eq. (1.3′). The crossover from the good solvent regime in the dilute region to the semidilute region takes place at

$$c^* \sim v^{-\frac{d}{d+2}} N^{-\frac{2(d-1)}{d+2}} . \tag{2.15}$$

3. Discussion

The before-mentioned blob concept is based on the picture of spatial correlation of the segment density. However, the average segment density $\rho(r)$, used in this article, at the distance r from one end of the chain is a more intuitive picture.

$\rho(r)$ itself is a decreasing function of r for either good solvents or the θ-solvent, while the number $\frac{ds}{dr} dr$ of segments, which are located in the range of $r \sim r+dr$, is an increasing function of r. As far as $d<4$, $\rho(r)$ as well as $\frac{ds}{dr}$ are smaller in good solvents that in the θ-solvent, and this reflects an expansion of the chain extension owing to the excluded volume effect.

In the semidilute region, it is very desirable to calculate directly the $\frac{d\psi}{ds}$ term in Eq. (2.2), which leads to Eqs. (2.13) and (2.14). However, in order to do this a specific approximation, far better than the Flory-Huggins one, must be needed.

This article is dedicated to Professor Michio Kurata, the former Director of the Institute for Chemical Research, Kyoto University, in sincerest appreciation of his continuous leadership in polymer science research.

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